Supporting Information for:

Stability and Porosity Enhancement Through Concurrent Ligand Extension and SBU Modification

Daofeng Sun, Yanxiong Ke, Tracy M. Mattox, Sean Parkin, and Hong-Cai Zhou*
Department of Chemistry and Biochemistry, Miami University, Oxford, OH 45056, USA

Experimental Section

Materials and Methods. All starting materials were obtained commercially and used without further purification. Thermal gravimetric analyses (TGA) were performed under N_2 on a PerkinElmer TGA 7 analyzer. A Beckman Coulter SA 3100 surface area analyzer was used to measure gas adsorption. Solution NMR spectra were collected on a Bruker 200 MHz spectrometer. Elemental analyses (C, H, and N) were performed by Canadian Microanalytical Services, Ltd.

Synthesis of tri-(p-bromophenyl)-benzene and 4-methoxycarbonylphenylboronic acid were carried out according to literature procedures.[1-3]

Synthesis of 1,3,5-tris(4′-methoxycarbonyl[1,1′-biphenyl]-4-yl-)benzene. To a 500 mL Schlenk flask was added 6 g 4-methoxycarbonylphenylboronic acid, 6.03g tri-(p-bromophenyl)–benzene, 9 g CsF, and 0.5 g $Pd(PPh_3)_4$ followed by 300 mL of degassed 1,2-dimethoxyethane. The solution was allowed to reflux under nitrogen for 48 hours and dried on a rotary evaporator. Approximately 100 mL H_2O was added and the compound extracted with $CHCl_3$. The organic phase was eluted with chloroform through a short silica column and dried to yield a light yellow powder. ^1H

NMR ($CDCl_3$): 3.94, 3H; 7.70-7.84, 6H, 7.88, 1H, 8.13, 2H.

Synthesis of 1,3,5-tris(4′-carboxy[1,1′-biphenyl]-4-yl-)benzene. 2 mL concentrated NaOH solution was added to a suspension of 3 g 1,3,5-tris(p-(4-methoxycarbonyl)biphenyl)benzene in 100 mL THF/MeOH (v:v = 1:1) and the mixture allowed to stir overnight. The pH value was adjusted to about two using concentrated HCl. The white solid was collected by filtration, washed with water and dried under vacuum.

Synthesis of $Zn_4(OH)_2(H_2O)_2(py)_2(TCBPB)_2 \cdot 3DMF \cdot py \cdot 3H_2O$ (1). A mixture of $Zn(NO_3)_2 \bullet 6H_2O$ (0.015 g, 5.0×10^{-5} mol), H_3TCBPB (0.0025 g, 3.77×10^{-6} mol) and pyridine (0.025 mL) in DMF, ethanol and water (1.5 mL, v/v = 5:2:1) was sealed under vacuum in a Pyrex tube. The tube was heated to 85°C, held for 24 hours, and cooled to room temperature at a rate of 0.1 °C/min. The resulting colorless crystals were washed with a mixture of DMF, ethanol and water (v/v = 5:2:1) to give **1** (0.002 g). Yield: 48.8%. Elemental analysis calcd (%) for **1**: C 63.11, H 4.74, N 3.87; found: C 60.46, H 4.50, N 3.96%.

Synthesis of $Zn_8(OH)_4(TCBPB)_4 \cdot 2DMF \cdot EtOH \cdot 3H_2O$ (2). Complex **2** was prepared as complex **1**, with triethylamine (0.025mL, 5% in ethanol) in place of pyridine, and a reaction temperature of 100 °C for 48 hours. The resulting block colorless crystals were washed to give **2** (0.0015 g). Yield: 45.5%. Elemental analysis calcd (%) for **2**: C 64.66, H 3.98, N 0.80; found: C 62.26, H 3.71, N 1.12%.

X-Ray diffraction studies. Single crystal X-ray diffraction was performed on a

Bruker SMART CCD diffractometer equipped with Mo Kα radiation for **1** and Cu K_α radiation for **2**. Raw data collection and cell refinement were done using SMART; data reduction was performed using SAINT+ and corrected for Lorentz and polarization effects.[4] Structures were solved by direct methods with SHELXTL and refined by full-matrix least-squares on F^2 using SHELX-97.[5] Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. Hydrogen atoms were placed in calculated positions with isotropic displacement parameters set to 1.2 × U_{eq} of the attached atom. The solvent molecules in **1** and **2** are highly disordered, and attempts to locate and refine the solvent peaks were unsuccessful. Contributions of scattering due to these solvent molecules were removed using the SQUEEZE routine of PLATON; structures of **1** and **2** were then refined again using the data generated.[6]

References.

1. Plater, M. J.; Mckay, M.; Jackson, T. *Perkin 1* **2000**, *16*, 2695.
2. Kotha, S.; Kashinath, D.; Lahiri, K.; Sunoj, R. B. *Eur. J. Org. Chem.* **2004**, 4003.
3. Chen, S. L.; Xu, C. G.; Zhao, K. Q.; Hu, P. *Sichuan Shifan Daxue Xuebao* **2000**, *23(5),* 511.
4. *SAINT+*, Bruker Analytical X-Ray Systems, Inc., Madison, WI, **2001.**
5. Sheldrick, G. M. *SHELX-97*, Bruker Analytical X-Ray Systems, Inc., Madison, WI, **1997.**
6. Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7-13.

Supporting Figures:

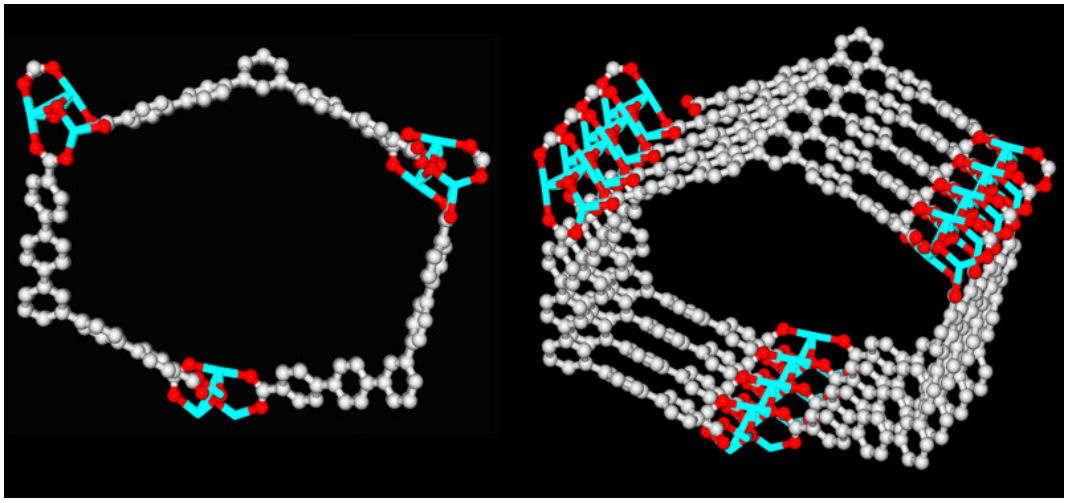

Figure S1. View of the left-handed helical chain in **1** formed by TCBPB ligands connecting different zinc atoms in the [010] direction (left) and approximate [010] direction (right).

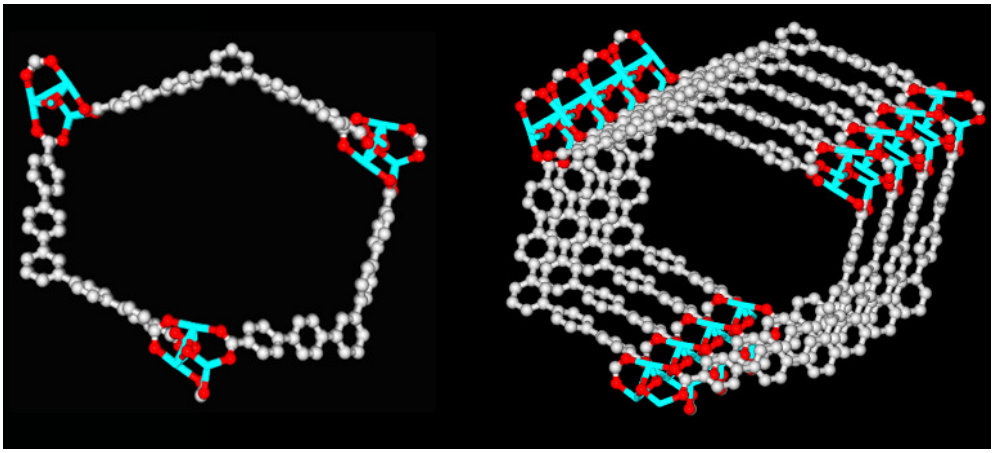

Figure S2. View of the right-handed helical chain in **1** formed by the TCBPB ligand connecting different zinc atoms in the [010] direction (left) and approximate [010] direction (right).

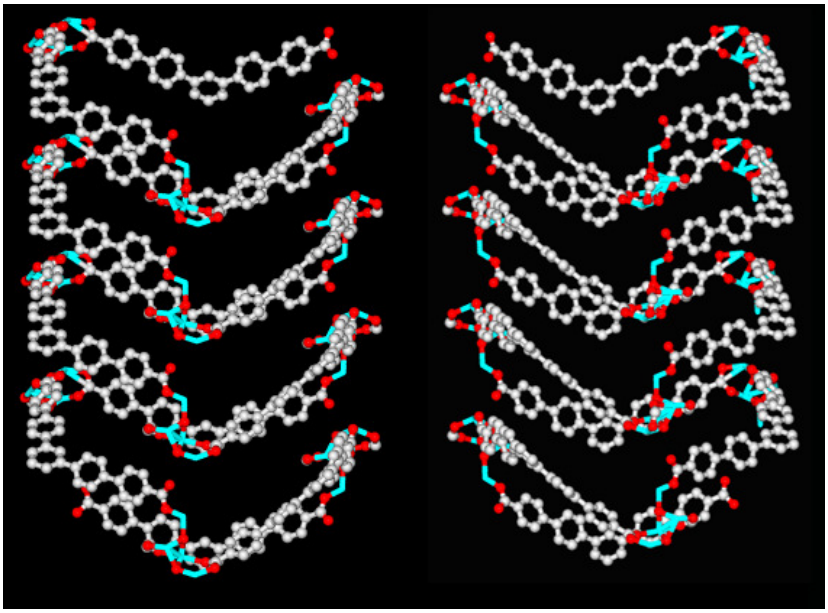

Figure S3. View of the left- and right-handed helical chains in **1** formed by TCBPB connecting different zinc atoms.

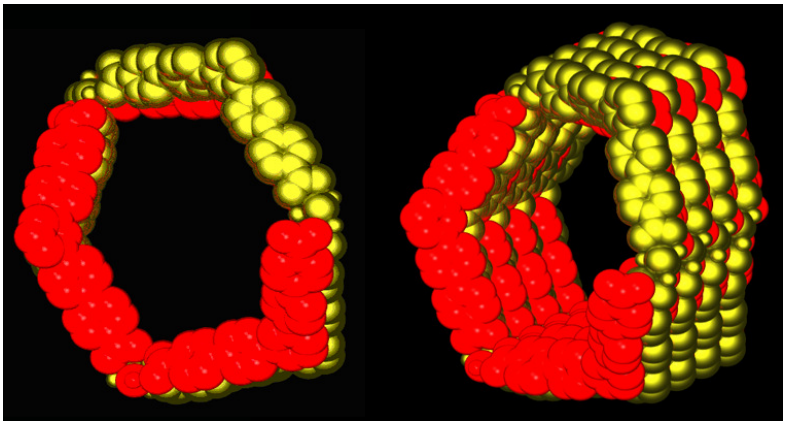

Figure S4. View of double helical chains in **1** formed by TCBPB connecting different Zn atoms in the [010] direction (left) and approximate [010] direction (right). Every TCBPB1 ligand connects Zn1, Zn2 and Zn3 while every TCBPB2 ligand connects Zn1, Zn2, Zn3 and Zn4 to form left or right-handed helical chains. Every two same-handed helical chains formed by TCBPB1 and TCBPB2, respectively, create a double helical chain by sharing Zn1, Zn2, Zn3 and the μ_3-OH groups.

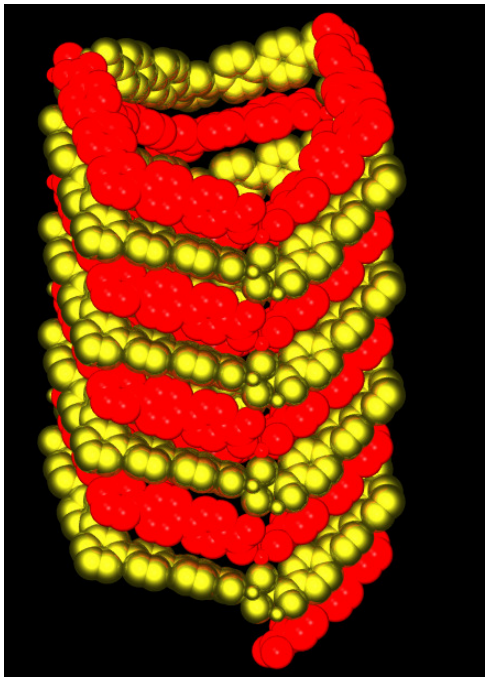

Figure S5. View of the double helical chains in **1** formed by TCBPB connecting different zinc atoms in the approximate [001] direction.

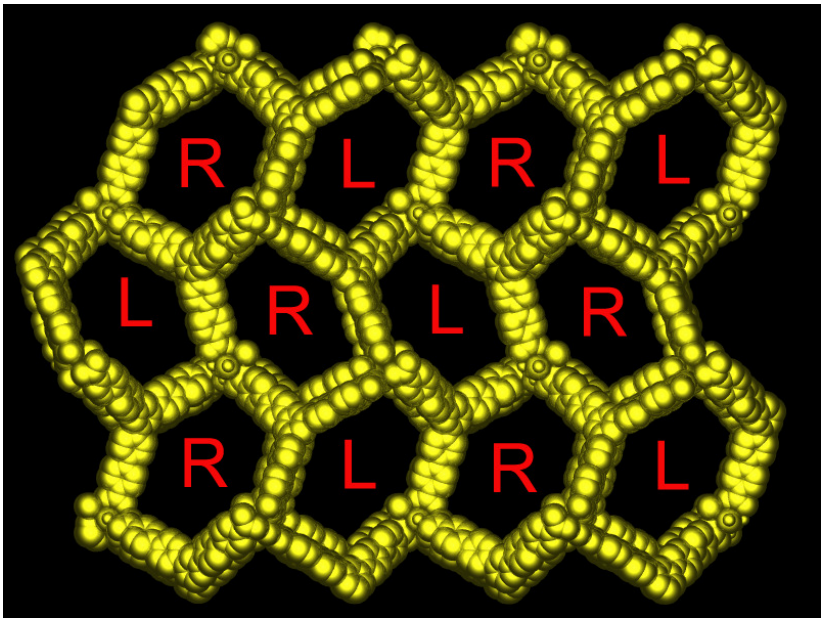

Figure S6. 3D porous framework with helical channels in **1** along [010] direction. Every ligand acts as the rim of three helical chains.

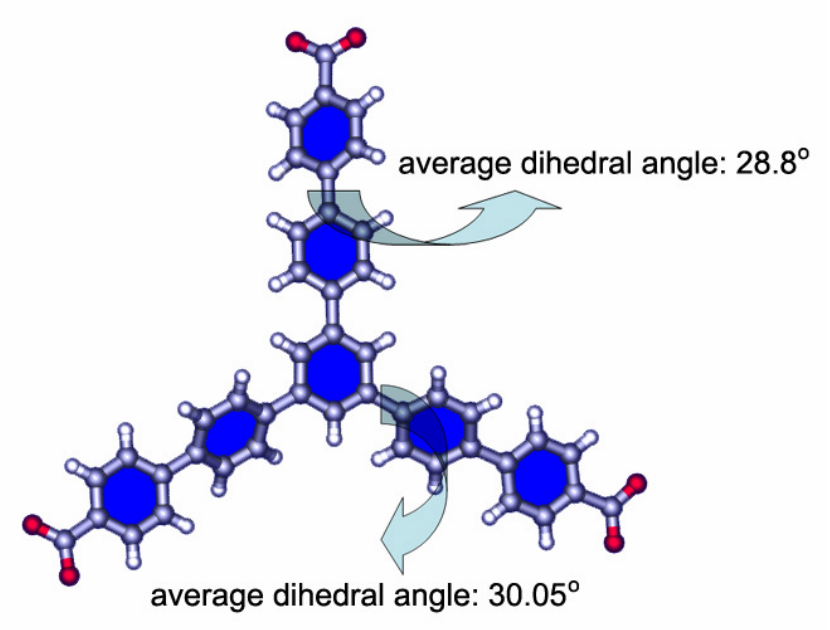

Figure S7. The non-planar TCBPB ligand in **1**. Due to C-H bond repulsions, there are large dihedral angles between the two peripheral rings, and between the central and peripheral rings.

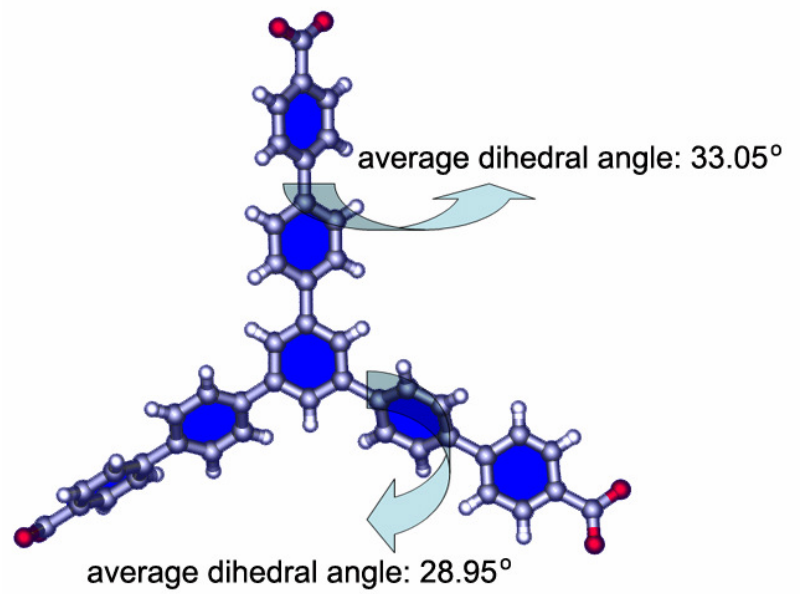

Figure S8. View of non-planar TCBPB in **2**.

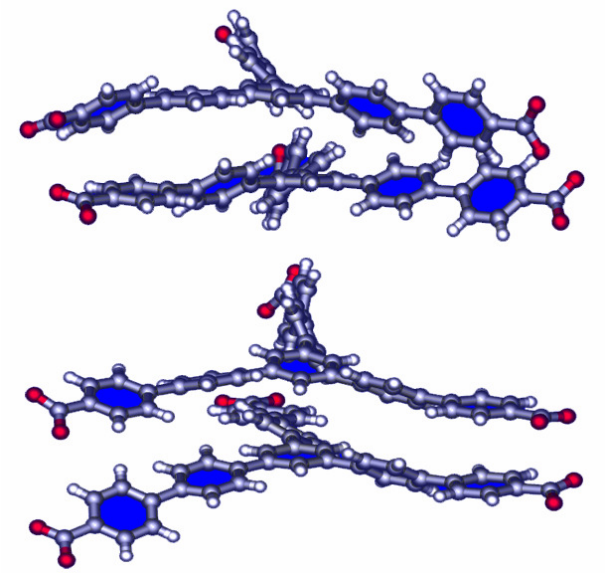

Figure S9. View of TCBPB pair in **1** (top) and **2** (bottom). Due to the ligand's non-planarity, there are no strong π--π interactions.

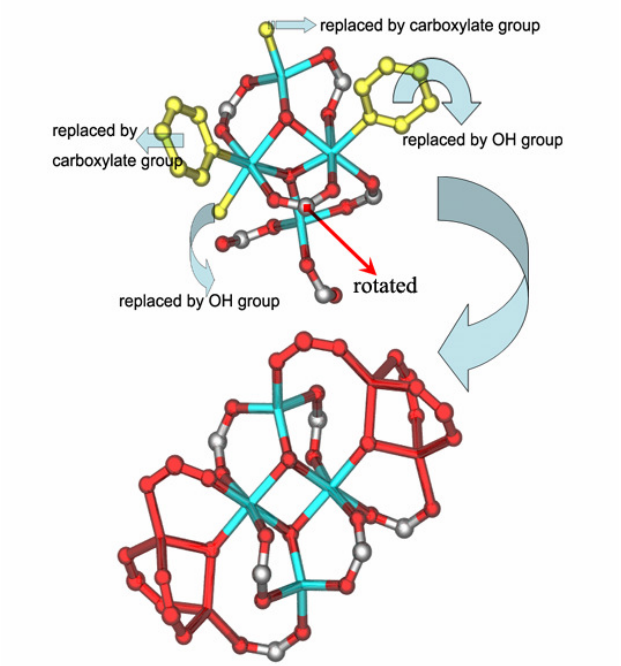

Figure S10. Relationship between the tetrahedral SBU in **1** (top) and the butterfly SBU in **2** (bottom). The tetra-nuclear SBU in **1** is transformed to the "butterfly" SBU in **2** when the coordinated pyridine or water molecules are replaced by μ_3-OH and carboxylate groups.

Nitrogen Adsorption Measurement for 2

A BERKMAN COULTER SA3100 surface area analyzer was used to measure N_2 isotherms. As-synthesized **2** was exchanged with MeOH to remove DMF solvates from the pores, then dried at 100 °C under vacuum for 12 hours to produce a solvent-free sample. A sample of solvent-free **2** (31 mg) was used for the BET measurement. Internal lines of the instrument were flushed by utilizing the "flushing lines" function of the program before measurement. (Adsorption data of N_2 is listed in Table S1.) The BET surface area of **2** was found is 758 m^2/g (calcd from the data of $0.05 < P/P_0 < 0.2$).

Table S1. Volumetric N_2 adsorption data of **2** at 77K.

Pressure (P/P_0)	Adsorption (cm^3/g, STP)	Pressure (P/P_0)	Adsorption (cm^3/g, STP)	Pressure (P/P_0)	Adsorption (cm^3/g, STP)
0	0	0.5203	232.837	0.9555	247.420
0	0	0.5601	233.777	0.9439	246.788
0	0	0.6000	234.726	0.9321	246.228
1E-4	49.568	0.6404	235.701	0.9149	245.388
2E-4	68.908	0.6600	236.244	0.8976	244.538
2E-4	90.159	0.6803	236.740	0.8802	243.743
4E-4	113.666	0.7002	237.283	0.8629	242.955
6E-4	134.443	0.7204	237.824	0.8455	242.221
0.0011	155.900	0.7405	238.361	0.8341	241.751
0.0027	178.213	0.7601	238.944	0.8192	241.166
0.0106	196.984	0.7803	239.532	0.8063	240.734
0.0274	206.810	0.8001	240.120	0.7945	240.317
0.0368	209.587	0.8130	240.490	0.7791	239.859
0.0465	211.741	0.8245	240.883	0.7661	239.475
0.0595	213.894	0.8356	241.250	0.7543	239.162
0.0669	214.947	0.8500	241.780	0.7391	238.766
0.081	216.552	0.8629	242.200	0.7192	238.259
0.1013	218.403	0.8744	242.685	0.6991	237.733
0.1193	219.732	0.8851	243.113	0.6794	237.275
0.1393	221.005	0.9003	243.755	0.6591	236.798
0.1597	222.096	0.9125	244.367	0.6391	236.360
0.1799	223.072	0.9237	244.985	0.6194	235.887
0.2001	223.940	0.9343	245.573	0.5994	235.452

0.2400	225.397	0.9450	246.196	0.5790	234.998
0.2798	226.692	0.9551	246.803	0.5593	234.622
0.3196	227.845	0.9697	247.694	0.5394	234.200
0.3603	228.936	0.9801	248.364	0.5195	233.790
0.4001	229.978	0.9889	248.957	0.4991	233.403
0.4406	230.964	0.9969	249.621	0.4796	232.930
0.4805	231.892	0.9675	248.078	0.4509	232.279
				0.3985	231.269